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LINEAR AND STAR-BRANCHED SILOXY-SILANE POLYMERS: ONE-POT A-B POLYMERIZATION AND END-CAPPING. Ralph M. Bozen, Lon J. Mathias, Department of Polymer Science, University of Southern Mississippi, Hattiesburg, MS 39406-0076.

A-B monomers were synthesized containing one alkene and one Si-H group per molecule. 3-Propenylidimethylsiloxydimethylsilane and 8-octenylidimethylsiloxydimethylsilane were obtained in good yield by interfacial reaction of the alkenyldimethylchlorosilane and dimethylsilylchloride in ether with buffer solution. Polymerization involved hydrosilation with chloroplatinic acid or the more reactive divinyltetramethyl-disiloxane platinum complex (Ashby's catalyst). Homopolymerization with an end-capping group gave linear polymer which can react with a core containing Si-H groups to give star polymers by a convergent approach. The core of tetrakis(dimethylsiloxy)silane with monomer polymerized to give stars with terminal Si-H groups which with olefins such as allyl phenyl ether would end-cap the star. Polymerization with 2-armed (tetramethyldisiloxane) gave linear polymers with terminal Si-H groups capable of end-capping with a variety of alkenes. Polymer characterization by ¹H, ¹³C and ²⁹Si NMR confirmed repeat unit structure and allowed estimation of number-average molecular weights of 2,400 to 6,500 by ¹H integration. Size-exclusion chromatography molecular weights (with respect to styrene standards) were comparable to or somewhat smaller, and both values were less than those predicted based on the ratio of star-core to monomer..

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Linear and Star-branched Siloxy-silane Polymers: One-pot A-B Polymerization and End-capping

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Introduction

Silane and siloxane polymers form an important family of commercial materials. They possess a unique combination of thermal stability, hydrophobicity, and segmental mobility which gives them low temperature flexibility and properties useful in demanding application where their high cost is justified.¹ Recent reports of silicone dendrimers^{2,3} make available large-molecule structures which greatly extend these potential uses. We have developed an alternative approach to siloxy-silane hyperbranched polymers that uses an A-B_n monomer possessing one alkene moiety and n Si-H groups.⁴ Addition of a platinum hydrosilation catalyst leads to the formation of polymer (ca 10,000-20,000 molecular weight) with a high active content of terminal Si-H groups that can be reacted (end-capped) with a variety of alkenes such as allyl phenyl ether and the allyl ether-anomethyl ether of oligooxyethylene.⁵

Application of the same general approach is possible using A-B and B_n monomers incorporating various alkene groups and substituted Si-H moieties.⁶ The A-B monomer has been synthesized by the condensation of alkenylchlorosilane and dimethylchlorosilane. (Scheme 1). Polymerization monomer and a B_n functional group with Ashby's catalyst⁷ gave star polymers by divergent synthesis. This allows the formation of the star polymers where the growing arms have a terminal Si-H functionality. The positive approach to star formation has also been investigated. Polymerization of monomer with an end-capping group gave linear polymers which can be attached to the node to give convergent stars formation.

Experimental

Monomer Synthesis

A round bottom flask with stirring bar was sealed with a rubber septum and purged with nitrogen. 1-octenylidimethylchlorosilane (18.55 g, 0.091 mol) and dimethylchlorosilane (11.94 g, 0.13 mol) were introduced into the flask via a glass tip needle using nitrogen pressure to keep the system under inert atmosphere. Diethyl ether was used as solvent and 50 ml of a 0.06 M LiHPO₄/KH₂PO₄ buffer solution was added to initiate the condensation of chlorosilanes. The desired A-B monomer was obtained in 92% yield, 84% purity (by gc) with 16% impurity due to isomerized alkene groups.

Polymer Synthesis

A round-bottom flask with 20 ml of xylenes was purged with nitrogen. Monomer (3.43 g, 0.014 mol) and allyl phenyl ether (0.41 g, 0.0031 mol) were added into the flask and three drops of a 1×10^{-3} M solution of Ashby's catalyst was added to initiate polymerization. After complete disappearance of Si-H groups by NMR, the arms for the convergent approach to star synthesis were purified to remove the catalyst by adding 3 g of EDTA and stirring in hexane for 1 day. The solids were filtered and solvent evaporated. The polymer arms (0.54 g, 0.00043 mol) and tetrakis(dimethylsiloxysilane) (0.042 g, 0.00013 mol) were injected into a septum-sealed NMR tube. One drop of a 5×10^{-4} M solution of Ashby's catalyst was introduced. ¹H NMR spectra were obtained at different time intervals. Upon complete reaction, the catalyst was removed from the system.

The divergent synthesis was performed in a dry, septum-sealed NMR tube with monomer (0.63 g, 0.0027 mol) and tetrakis(dimethylsiloxysilane) (0.035 g, 0.00011 mol). Two drops of a 5×10^{-5} M solution of Ashby's catalyst is introduced. After reaction completion, allyl phenyl ether was added in excess to end-cap the star polymer. The catalyst was removed by the same procedure listed above.

Results and Discussion

Conversion of silyl chloride 1a to monomer 2a occurred in good yield. Homopolymerization gave linear polymer 3 along with substantial amounts of cyclic product 4. Although the latter was isolated in ca 25% yield, it did not interfere with formation of reasonable molecular weight polymer. This cyclization reaction can, however, have a substantial impact on the formation of hyperbranched polymers since it would terminate the low-concentration alkene end of the growing polymer through intramolecular addition.⁸

Synthesis of 2b from 1b was complicated by the unexpected presence of two impurities (ca 6 and 10%) in the commercial starting material¹⁰ possessing internal double bonds presumably arising from isomerization of the terminal double bond. These impurities lead to isomers of 2b that could not be removed. Homopolymerization gave linear material with residual internal groups as well as the desired terminal alkenes (Figure 1, inserts) with ¹H peaks at 5.3 and 4.9 ppm, respectively. The peak at 3.9 ppm is from CH₂ groups adjacent to the phenyl ether while two sets of sharp peaks in the insert at 6.8 and 7.20 ppm are from phenyl rings from end-capping with allyl phenyl ether. Extended reaction time (three days to two weeks) resulted in only partial disappearance of the internal alkenes despite the initial very rapid reaction of terminal alkene units (ca, a few minutes). The SEC trace gave peaks that correlate to arm lengths of 1-3, plus a more intense broad peak for arm lengths of 4-9 (estimated from polystyrene standards). ¹H NMR integration gave an average arm length of 4.6 which was lower than the SEC retention time for the major peak. The discrepancy in the calculations may be due to the difference in reactivity of the internal vs terminal double bond terminating the polymerization. With the presumed step-growth nature of the polymerization, slow reacting impurities would act as chain stoppers.

The core species was added to the arm reaction mixture along with catalyst. Complete disappearance of the terminal double bonds (Figure 1, top trace) and Si-H groups at 4.7 ppm (of added core material) was observed within 24 h. Linear polymer (with internal double bonds) was still present in the SEC trace along with polymer with a molecular weight of 6,800 consistent with star polymer formation.

The divergent approach involved polymerization in the presence of tetrakis(dimethylsiloxysilane) to give star polymer 5 that possessed terminal Si-H groups capable of further reaction. Allyl phenyl ether addition to the polymer solution with still-active catalyst gave the end-capped product 6. Figure 2 gives the ¹H spectra of monomer-plus-node mixture (lower trace) and polymerization mixture at various conversions. The peaks around 7 ppm are from solvent in the catalyst solution. The concentration of the solvent remains constant, so reaction can be monitored by relative peak intensity. The top trace is of the end-capped polymer with catalyst removed. The residual peaks at 5.3 ppm show a small amount of residual linear polymer with less reactive internal double bonds. The SEC trace gave a molecular weight slightly higher than from NMR integration.

Figure 3 presents ¹H spectra that focus on the methyl hydrogens attached to silicon. At 0.27 and 0.22 ppm are doublets of methyl hydrogens coupled to Si-H moieties of the core and monomer, respectively. Disappearance of the core peaks (labeled a) shows that substitution occurs at all four arms, plus there is a shift for the methyl hydrogens to 0.135 ppm (peak c) upon incorporation into the polymer. Since the backbone methyl hydrogens of both silicones are now identical, there is a decrease in the monomer methyl hydrogen at 0.11 ppm (labeled d) and concomitant increase in the 0.098 ppm peak (labeled e). Residual peaks at 0.11 ppm and 0.22 ppm are from end-group methyls.

SEC analysis of polymer 6 gave a retention time corresponding to polystyrene of molecular weight 5,400 while ¹H NMR integration of end-capping groups versus repeat units gave a number average value of 3,250. The star nature of this polymer is expected to give a more compact structure in solution that should lead to a lower molecular weight estimate by SEC than for a corresponding linear polymer. Molecular weight distributions for the linear polymers and star polymers made with this method were broad (ca 2 or greater) probably due to the (presumed) step-growth nature of the polymerization coupled with an expected nonhomogeneous distribution of catalyst particle sizes (which would effect rapid migration of the catalyst particles) and the broadening due to the internal double bonds acting as premature terminating groups due to their reduced reactivity.

The star nature of these materials might be questioned based on a difference in reactivity of the core Si-H groups versus the monomer Si-H. We have carried out extensive model compound reactions which confirm the rapid reaction of the core units and high-yield formation of tetrasubstituted derivatives from hydrosilation of the core species with various alkenes. We have also observed side-reactions with water, for example, involving hydrolysis of Si-H groups and formation of Si-O-Si units which would effectively crosslink the star polymers. These reactions can be controlled by careful drying and maintenance of an inert atmosphere during polymerization, and their occurrence easily monitored spectroscopically.

We conclude that both propenyl and octenyl monomers polymerize well although each suffers from a drawback: cyclization of the propenyl

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nomer and the presence of internal and less reactive alkenes in the aryl compound. Elimination of the latter should make 2b a general monomer for a wide variety of linear, star and even comb-branched polymers which combine unique physical properties (hydrophobicity, very low T_g 's, good chemical and thermal stability) with potential for end-group functionalization leading to novel applications as single-molecule reactors, artificial blood and precursors to ideal siloxy-silane networks.

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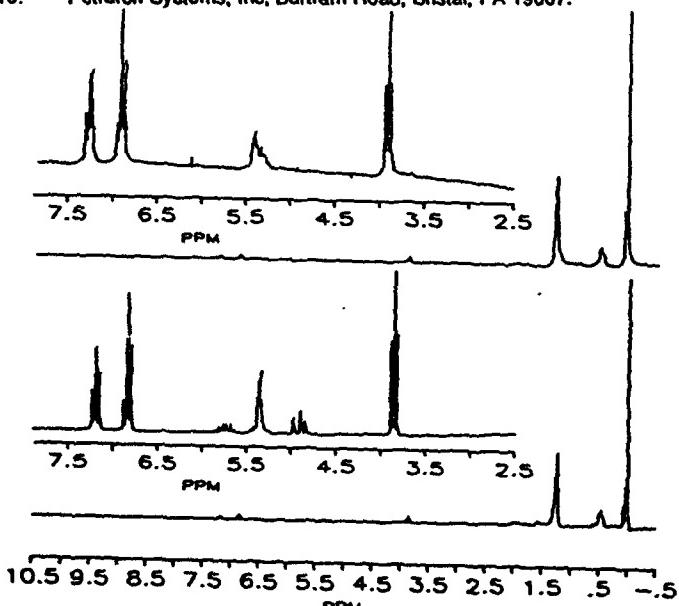


Figure 1. ^1H NMR spectra in CDCl_3 of arms 2b full scale (bottom trace) and expanded inset; star polymer and expanded inset (top trace).

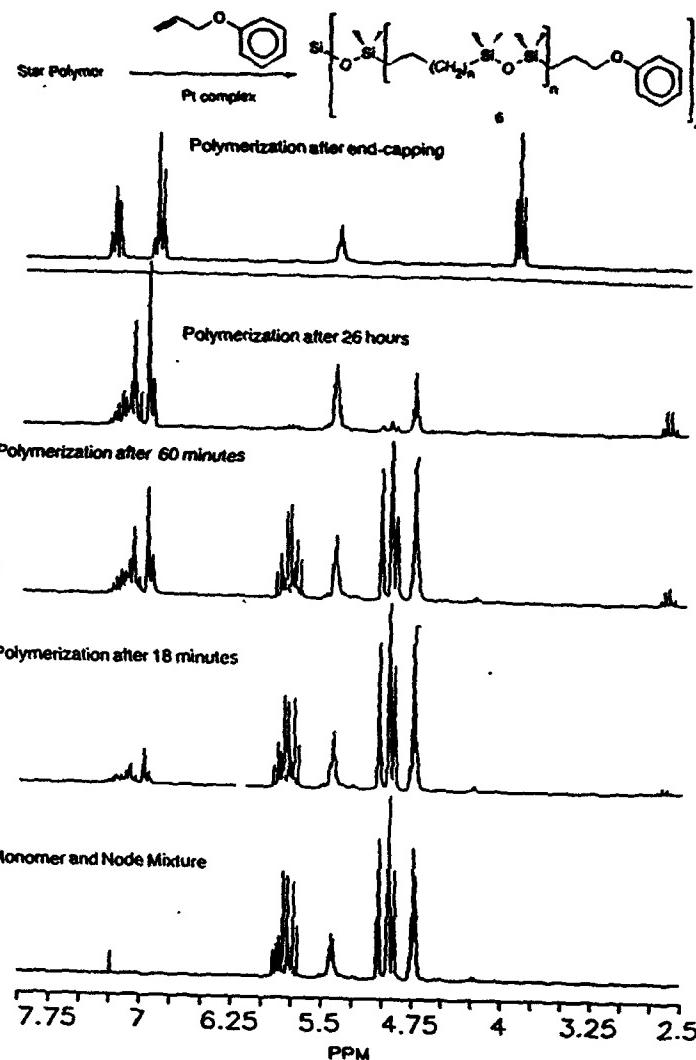
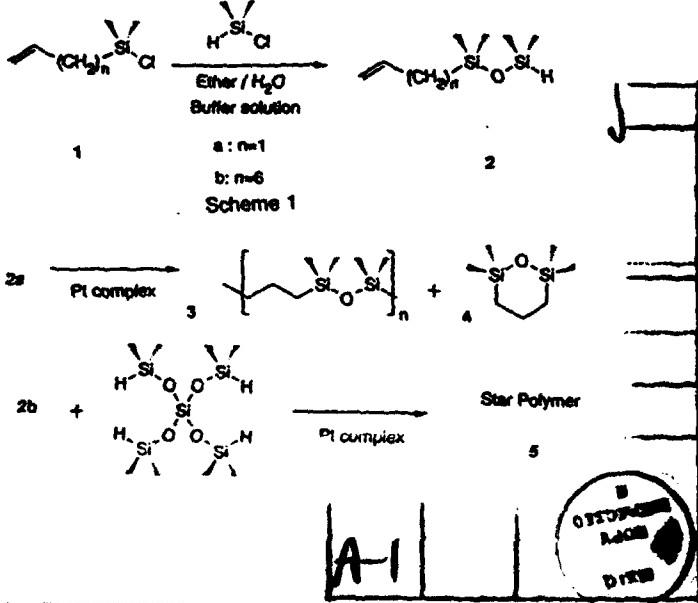


Figure 2. ^1H NMR spectra in CDCl_3 of monomer 2b and node (bottom trace); polymerization at 18 min, 60 min, 25 hours and 2 days after addition of allyl phenyl ether cleaned of Ashby's catalyst (from second-to-bottom up).

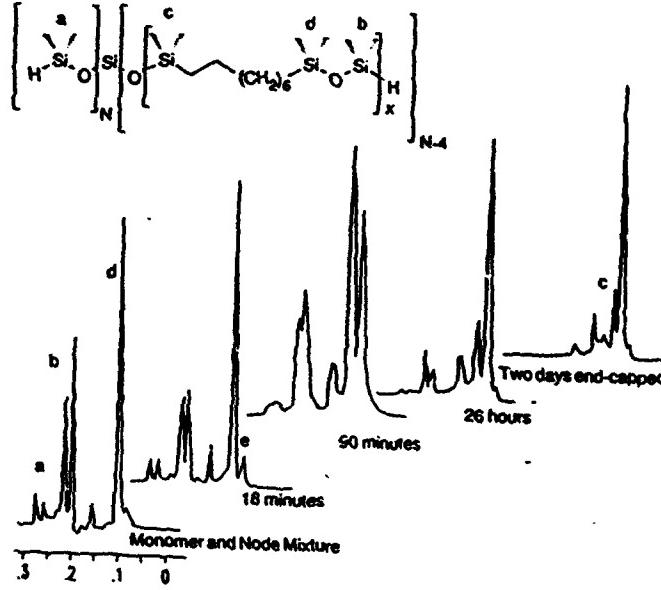


Figure 3. ^{1}H NMR spectra in CDCl_3 of monomer 2b and node (bottom track) of the Methyl hydrogens attached to silicon; polymerization at 1 min, 60 min, 26 hours and 2 days after addition of allyl phenyl ether cleaned of Ashby's catalyst (from second-to-bottom up).